RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 38, NUMBER 11 15 OCTOBER 1988-I

Hydrostatic and uniaxial pressure coefficients of CdTe

D. J. Dunstan* and B. Gil
Groupe d'Études des Semiconducteurs, Université des Sciences et Techniques du Languedoc, Place Eugene Bataillon-34060 Montpellier-Cedex, France

K. P. Homewood
Department of Electronic and Electrical Engineering, University of Surrey, Guildford, Surrey, GU2 5XH, United Kingdom

(Received 6 June 1988)

The pressure dependence of direct band-gap CdTe has been measured by observing the direct exciton photoluminescence and donor-acceptor pair photoluminescence under hydrostatic pressures up to 35 kbar. A value of 6.5 ± 0.2 meV kbar^{-1} was obtained corresponding to a hydrostatic deformation potential $\Xi = 2.74 \pm 0.09$ eV. Using this value, the uniaxial stress data of Thomas [J. Appl. Phys. **32**, 2298 (1961)] is reassessed to determine a best value of $\Delta = 8.7 \pm 0.3$ meV kbar^{-1}, corresponding to $D_u = 1.11$ eV and $D_{u'} = 2.57$ eV.

The growth of semiconductors and heterojunctions by molecular-beam epitaxy has stimulated the development of new classes of materials because of the extremely large number of combinations that are possible, and the extent to which the transport and optical properties of these semiconductors can be modified to tailor them to specific device applications. Among these combinations are II-VI CdTe-ZnTe strained-layer quantum wells and superlattices; they actually constitute a rapidly developing field of semiconductor physics.[1-4] These systems are not lattice matched so that there are large axial strains in the different layers of the heterostructure, which can be resolved into uniaxial and hydrostatic components. The ability to tune independently the transport properties of the carriers and the conduction- and valence-band discontinuities in such heterostructures requires the knowledge of the bulk material properties and their dependence on axial and hydrostatic strain. In particular, the valence-band heavy-hole–light-hole (HH-LH) splitting under uniaxial strain and the hydrostatic pressure dependence of the Γ_6^c-Γ_8^v direct band gap need to be known to some accuracy. For ZnTe the data in the literature are relatively complete.[5] In contrast, the values of these important quantities in CdTe are not at all clear. From uniaxial stress measurements on the exciton reflectivity peaks, Thomas[6] gave a first estimate of the HH-LH splitting. He proposed an average value of 13.9 meV kbar^{-1} for both [001] and [111] stress. The shift of the center of gravity of the spectrum gave a hydrostatic pressure shift dE_g/dP of roughly 11 meV kbar^{-1}. However, subsequent direct determinations of dE_G/dP gave values of ~ 8 meV kbar^{-1}.[7,8] These measurements were carried out in hydraulic pressure systems where accurate high-pressure calibration is far from trivial. Since the advent of diamond-anvil high-pressure cells and the ruby fluorescence pressure scale,[9,10] optical spectroscopy under accurate high pressure has become relatively straightforward. We have, therefore, made a redetermination of the CdTe dE_g/dP in a diamond anvil high-pressure cell (DAC), at 2 K with argon as the pressure transmitting medium. Note that much of the older DAC work in the literature used alchohol as the pressure transmitting medium: this is satisfactory at 300 K up to ~ 100 kbar but can lead to axial strains and errors in the pressure in the sample of as much as 5% or 10% at low temperatures.[11]

A CdTe sample was cleaved to the required dimensions ($\sim 50 \times 100 \times 30$ μm^3) and mounted in a miniature cryogenic DAC (Ref. 12) together with a piece of ruby for pressure calibration. The cell was filled with argon by cooling to 80 K under an Ar atmosphere at 6 bars and then closing the cell. Photoluminescence measurements were made in a He-bath cryostat at about 2 K. Excitation was provided by ~ 20 mW of 514.5-nm argon laser radiation, and the luminescence was analyzed by a 1.5-m THR Jobin Yvon spectrometer and detected by a photomultiplier. The spectra were not corrected for system response.

Typical spectra are shown in Fig. 1. At 0 kbar, the edge emission is dominated by the A^0X bound exciton line [Fig. 1, curve (a)]. At lower energy the A^0X-1 LO phonon replica and two weak donor-acceptor pair (DAP) bands can be seen. As the pressure is raised, the A^0X line is rapidly quenched, and the exciton edge emission band becomes weak and unresolved [Fig. 1, curves (b) and (c)]. One of the weak DAP bands retains its intensity and dominates the spectrum above a few kilobar. The reason for the quenching of the exciton edge emission and the DAP_2 band is not known.

Both the exciton and DAP_1 edge emissions bands could be followed up to 35 kbar [the phase transition of CdTe is reported to occur near 41 kbar (Ref. 13)]. Figure 2 shows the peak energies as a function of the pressure. Within experimental error, both bands shift linearly to higher energy with pressure at 6.5 meV kbar^{-1}. The error in the pressure calibration is due to the determination of the peak positions of the emission of the ruby in the cell and of a reference ruby placed on the exterior of the cell; these wavelengths were determined to ± 0.05 Å corresponding to an accuracy in the wavelength shift $\Delta\lambda$ of ± 0.1 Å. Using $P(\text{kbar}) = 0.365\Delta\lambda$ Å,[10] and taking the pressure homogeneity in the cell to be better than ± 0.2 kbar,[14] we

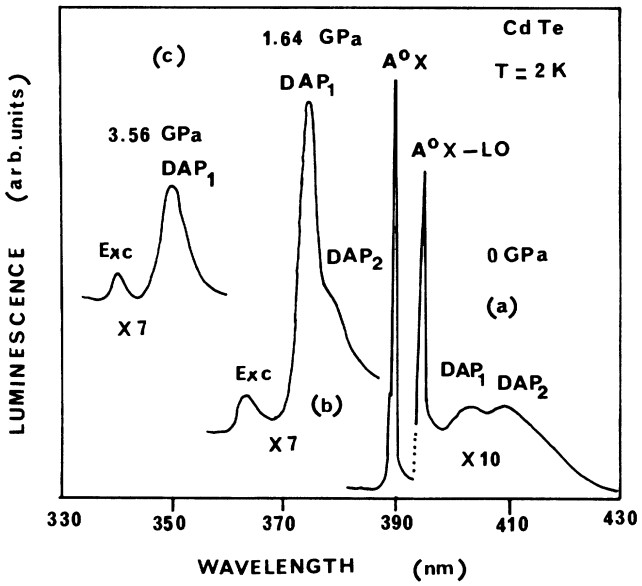

FIG. 1. Photoluminescence spectra collected at 2 K in the DAC at 0 kbar (a) and at higher pressures [(b) and (c)].

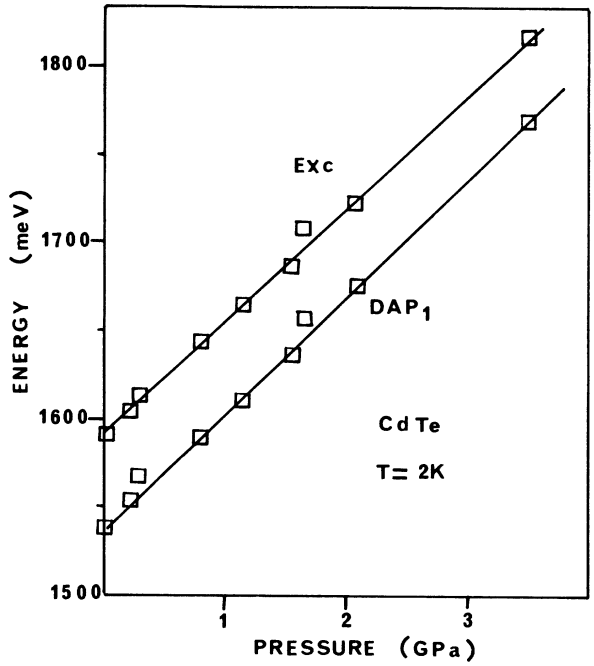

FIG. 2. Plot of the transition energies as a function of the hydrostatic pressure.

have $\Delta P = \pm 0.3$ kbar. The error in the determination of the CdTe emission peak energies is primarily due to the ambiguity in identifying the peak of a weak signal with poor signal-to-noise ratio (Fig. 1). The errors are indicated by the data points in Fig. 2. Neglecting the pressure dependence of the exciton and donor-acceptor binding energies, we conclude that the pressure coefficient of the direct band gap of CdTe may be given as 6.5 ± 0.2 meV kbar. This value is considerably lower than those reported previously (Table I). The discrepancy with Langer[7] and Babonas, Bendoryus, and Shileika[8] may be attributed to the improvement in hydrostatic pressure calibration with the introduction of the ruby scale. Our result falls within the range of theoretically predicted values[15-17] (see Table I); in particular, a close agreement is found with the recent calculation of Cardona and Christensen.[17]

Thomas[6] reported a wide scatter in his results in different samples and for different orientations of his external uniaxial stress (see Table II). A large part of this scatter was undoubtedly due to experimental difficulties in calibrating the uniaxial stress, and to uneven stress distribution in the sample. However, the center of gravity shift should be isotropic and constant in different samples, and so provides a calibration of the stress. Using our value of 6.5 meV kbar^{-1} for dE_g/dP, we have renormalized Thomas's data and thereby removed most of the scatter

TABLE I. Values of dE_g/dP obtained by various experimental and theoretical methods. The most recent theoretical results and the present experimental investigation are in close agreement.

dE_g/dP (meV kbar^{-1})	Method	Reference
11.4	Uniaxial-stress Reflectivity (2 K)	6
8.0 ± 0.2	Hydrostatic pressure Reflectivity (77 K) Absorption (77 K)	7
7.9 ± 0.2	Hydrostatic pressure Reflectivity (300 K)	8
8	Phillips-Van Vechten	15
2.8	Empirical-pseudopotential	16
6.45	Linear-muffin-tin-orbitals	17
6.5 ± 0.2	Hydrostatic pressure Photoluminescence (2 K)	This work

TABLE II. Light-hole–heavy-hole splitting under various orientations of the uniaxial stress. All values are expressed in meV kbar^{-1}.

Direction	$\theta=0$ [001]	$\theta=54°42'$ [111]	$\theta=90°$ [110]	$\theta=70°$
Splitting[a]	12.6–16.9	11.4–15.7	8.65–19.7	14.6–16.5
Average[a]	13.9	13.7	15.1	15.5
Shift[a]	1.7–2.8	2.8–3.9	2.0–4.3	3.8
Average[a]	2.1	3.5	3.7	3.8
Splitting[b]	12.9–16.5	7.4–9.5	7.9–9.2	8.2–9.4
Average[b]	(14.4)	(8.4)	8.9	8.8
Calculated[c]	14.4	8.4	10.2	9.2
Calculated[d]	8.7 ± 0.3	8.7 ± 0.3	8.7 ± 0.3	8.7 ± 0.3

[a]Experimental values from Ref. 6.
[b]Renormalized to $dE_g/dP=6.5$ meV kbar^{-1}.
[c]Fit to [001] and [111] experimental values.
[d]Isotropic fit to [111], [110], and 70° experimental values.

(Table II). Note that while Thomas concluded that the splitting was isotropic, in the renormalized data the [001] splitting is much larger than in the other three directions. The [001] splitting gives $D_u=1.83$ eV while the [111] data give $D_{u'}=2.57$ eV. On the other hand, the [111], [100], and 70° data are consistent with an isotropic splitting $\Delta=8.7$ meV kbar^{-1}, corresponding to $D_u=1.11$ eV and $D_{u'}=2.65$ eV.[18] There are three other observations which must be taken into account. First, as Thomas noted, the polarization properties of the reflectivity spectra are consistent with an isotropic splitting. Second, it has been observed that the heavy-hole transition energy is almost independent of the [001] biaxial stress: Dal'bo *et al.* studied the piezomodulated reflectivity of CdTe/(CdZn)Te structures with 3% and 8% zinc[4] and Magnea *et al.* measured the absorption spectra of strained CdTe epilayers on $Cd_{0.96}Zn_{0.04}Te$ substrates.[19] This observation provides a very precise, accidental, relationship between dE_g/dP and Δ_{001}:

$$dE_g/dP \sim \tfrac{3}{4}\Delta_{001},$$

implying $\Delta_{001}=8.7$ meV kbar^{-1}. Third, even after normalizing to the shift, the [001] data of Thomas are still exceptionally scattered (Table II). We therefore suggest that these data should be ignored, and that the best values currently available are $\Delta_{001}=\Delta_{111}=8.7\pm0.3$ meV kbar^{-1}. However, in view of the good fit reported by Magnea *et al.* between optical and x-ray data using $\Delta_{001}=13.9$ meV kbar^{-1},[19] it is evidently very desirable that the uniaxial stress splittings in CdTe should be remeasured, given the interest of the material.

In summary, from measurements of the band-edge photoluminescence of CdTe, we obtain $dE_g/dP=6.5\pm0.2$ meV kbar^{-1} and deduce a deformation potential $\Xi=(D_d^c-D_d^v)=2.74\pm0.09$ eV. A reassessment of uniaxial data[6,19] in light of this result gives $\Delta_{001}=\Delta_{111}=8.7\pm0.3$ meV kbar^{-1}, for the heavy-hole–light-hole splitting, corresponding to deformation potentials $D_u=1.11$ eV and $D_{u'}=2.65$ eV, although higher values for Δ_{001} and D_u cannot be ruled out.

We are grateful to the Science and Engineering Research Council (U.K.) and the Centre National de la Recherche Scientifique (France) for the financial support of this work. One of us (D.J.D.) thanks the University of Montpellier for its hospitality.

*Permanent address: Physics Department, University of Surrey, Guildford, Surrey, GU2 5XH, England.

[1]H. Mathieu, A. Chatt, J. Allegre, P. Lefebvre, and J. P. Faurie, Phys. Rev. B (to be published) and references therein.
[2]H. Mariette, F. Dal'bo, N. Magnea, G. Lentz, and H. Tuffigo, Phys. Rev. B (to be published).
[3]H. Tuffigo, R. T. Cox, N. Magnea, Y. Merle D'Aubigne, and G. Million, Phys. Rev. B **37**, 4310 (1988).
[4]F. Dal'bo, N. Magnea, G. Lentz, H. Mariette, B. Gil, J. Allegre, and H. Mathieu, Proceedings of the Nineteenth International Conference on the Physics of Semiconductors, Warsaw, 1988 (unpublished).
[5]This is reviewed in H. Strossner, S. Ves, Chul Koo Min, and M. Cardona, Solid State Commun. **61**, 275 (1987).
[6]D. G. Thomas, J. Appl. Phys. **32**, 2298 (1961).
[7]D. Langer, *Proceedings of the Seventh International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod, Paris, 1964), p. 241.
[8]G. A. Babonas, R. A. Bendoryus, and A. Yu. Shileika, Fiz. Tekh. Poluprovodn. **5**, 449 (1971) [Sov. Phys. Semicond. **5**, 392 (1971)].
[9]A. Jayaraman, Rev. Mod. Phys. **55**, 65 (1983).
[10]J. D. Barnett, S. Block, and G. J. Piermarini, Rev. Sci. Instrum. **44**, 1 (1973).
[11]M. Cardona (private communication); J. D. Lambkin (private communication).
[12]D. J. Dunstan and W. Scherrer, Rev. Sci. Instrum. (to be published).
[13]Kenneth Zanio, *Cadmium Telluride, Semiconductors and Semimetals, Volume 13* (Academic, New York, 1978), p. 10.
[14]M. Leroux, J. Leymarie, G Méheut, and G. Neu, Rev. Sci. Instrum. **59**, 627 (1988).

[15]D. L. Camphausen, G. A. N. Connel, and W. Paul, Phys. Rev. Lett. **26**, 184 (1971).

[16]Y. F. Tsay, S. S. Mitra, and B. Bendow, Phys. Rev. B **10**, 1476 (1974).

[17]M. Cardona and N. E. Christensen, Phys. Rev. B **35**, 6182 (1987).

[18]Here we use the notation of Kleiner and Roth [Phys. Rev. Lett. **2**, 334 (1959)]. The relationship with the notation of Bir and Pikus [*Symmetry and Strain-Induced Effects in Semiconductors* (Wiley, New York, 1974)] are $D_u = 3b/2$, $D_{u'} = \sqrt{3}d/2$, and $\Xi = a$.

[19]N. Magnea, F. Dal'bo, C. Fontaine, A. Million, G. P. Gaillard, Le Si Dang, Y. Merle d'Aubigné, and S. Tatarenko, J. Cryst. Growth **81**, 501 (1987).